An Investigation on Treatment of Bauxite through Hydrogen Plasma

Thesis submitted in partial fulfilment of the requirements for the award of the degree of

Master of Technology

in

Mechanical Engineering

[Specialization**:** Steel Technology]

Submitted by

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Under the supervision of

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CERTIFICATE

This is to certify that, the thesis entitled "**An Investigation on Treatment of Bauxite through Hydrogen Plasma**" being submitted to the National Institute of Technology, Rourkela by **Mr. Manish Sahu,** Roll no. 212MM2460 for the award of **M.tech degree** in **Steel Technology** at National Institute of Technology, Rourkela, is a bonafide record of research work carried out by him under my supervision and guidance. The experimental work and analysis of results are original work of the student and have not been presented anywhere for the award of a degree to the best of our knowledge.

In my opinion, the candidate has fulfilled all the prescribed requirements and the thesis is of standard required for the award of M.tech degree in Steel Technology.

Supervisor

Date: 26-05-2014

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Date: 22-05-2014 Roll no. - 212MM2460

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CONTENTS

ABSTRACT

Extraction of metals from their oxides is primarily extracted through pyrometallurgy, which uses carbon as major reducing agent. For using carbon have the limitations of future supply and environmental pollution. In order to avoid this problem hydrogen can be used as an alternative source of reducing agent for extraction of metals. From the Ellingham diagram it is also observed that hydrogen (H-H_2O & H^+-H_2O) is placed below almost all metal oxides (M-M_xO_y). Hence, in different extractive metallurgical processes hydrogen can be used as a standard reducing agent for the reduction of metal oxides. It has unique thermodynamic properties aiding the economic reduction process and its combustion product is water which is environmentally harmless unlike carbon oxides/carbon monoxide. In the present study an attempt has been made to investigate reduction of bauxite through hydrogen plasma and molecular hydrogen. For this purpose some experiments are being carried out for the reduction of Al_2O_3 present in bauxite by using hydrogen in form of plasma and also by molecular hydrogen. Further, constituents of reduced bauxite sample with hydrogen plasma and molecular hydrogen is separated by acid leaching. Reduced bauxite sample and separated constituent are characterized by X-ray diffraction technique. It is observed that only iron oxide present in the sample was reduced under the processing conditions.

Keywords: Ellingham diagram, Metal extraction process, Hydrogen plasma, Bauxite minerals.

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LIST OF ABBREVIATIONS AND SYMBOLS

LOI	Loss on ignition
XRD	X-ray diffraction
sccm	Cubic centimetre per second
ΔG	Gibb's Free Energy
ΔH	Change in enthalpy
ΔS	Change in entropy

CHAPTER-1

INTRODUCTION

1.1. Introduction

1.2. Objective

CHAPTER – 1

INTRODUCTION

1.1. Introduction:

In extractive metallurgy many metal oxides are reduced primarily with carbon for extraction of metals. The carbothermic reduction process produces a lot of CO_2 which is responsible for greenhouse effect. Also carbon has a limitation of future supply. It is, hence, more reasonable to find new technology with no or less carbon input. Many of current research and development programs are dedicated to finding innovative solution to decrease CO or CO_2 emissions produced by the industry. For minimising the emission of CO_2, now a day's hydrogen is used as a standard reducing agent in place of carbon for the reduction of different metal oxides. The reduction of metal oxides using hydrogen presents several potential advantages; (a) hydrogen is readily available, being the most abundant element in the universe; [1] (b) the reaction of metal oxides with hydrogen is far more environmentally friendly, as the by-product being water rather than carbon dioxide; (c) hydrogen in form of plasma (consisting of H and H^+) is a very powerful reductant that can reduce most metal oxides at temperatures below the melting point of metals [1]; (d) The most important advantages of using atomic instead of molecular hydrogen are that a substantial decrease in the reduction temperature can be expected. This can be especially significant for stable oxides, not reducible in hydrogen below the melting point of metal, such as Al_2O_3, SiO_2 etc. [2].

The aim of present work is to deepen our understanding of hydrogen plasma as an alternative for the reduction of bauxite ore. Bauxite ore contains Al_2O_3, Fe_2O_3, TiO_2 and SiO_2. In the Ellingham diagram the position of these oxides are shown in the fig.1.1. From the Ellingham diagram the observed standard free energy changes for the above oxides are given below [3];

$$4Fe_3O_2 + O_2 = 6Fe_2O_3, \quad \Delta G^o = -95\text{Kcal/mol} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (1.1)$$

$$Si + O_2 = SiO_2, \quad \Delta G^o = -203\text{Kcal/mol} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (1.2)$$

$$Ti + O_2 = TiO_2, \quad \Delta G^o = -205\text{Kcal/mol} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (1.3)$$

$$4/3Al + O_2 = 2/3Al_2O_3, \quad \Delta G^o = -252\ \text{Kcal/mol} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (1.4)$$

The standard free energy changes for the following reactions are [4]:

$$2H_2 + O_2 = 2H_2O, \qquad \Delta G^o = -114.35 \text{ Kcal/mol} \qquad \text{…...…… (1.5)}$$

$$4H + O_2 = 2H_2O, \qquad \Delta G^o = -307 \text{ Kcal/mol} \qquad \text{……... (1.6)}$$

$$4H^+ + O_2 + 4e^- = 2H_2O, \qquad \Delta G^o = -1540 \text{ Kcal/mol} \qquad \text{…..…….. (1.7)}$$

From the above equations it may be conclude that thermodynamically, the oxides present in bauxite can be reduced by hydrogen (H and H^+). The present study deals with reduction of bauxite through molecular hydrogen and hydrogen plasma.

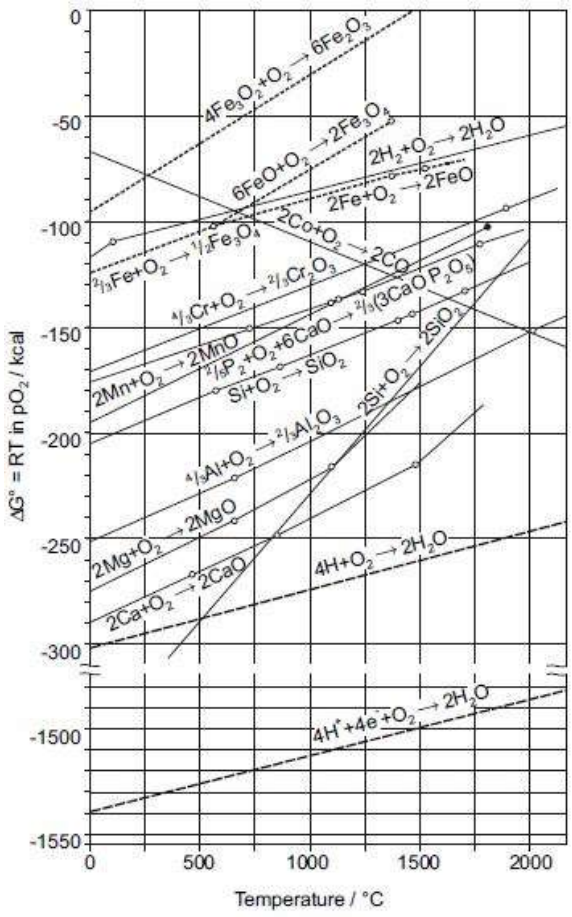


Fig. 1.1: Ellingham diagram of various oxides. [6]

1.2. Objective:

Objectives of the present work are;

- To investigate the reduction of bauxite through hydrogen plasma & molecular hydrogen, and understanding the thermodynamics of reduction.
- To separate the different constituents (metal/metal-oxides) after reduction.

CHAPTER-2

LITERATURE REVIEW

2.1. Bauxite Minerals

2.2. Aluminium Production

2.3. Ellingham Diagram

2.4. Plasma

2.5. Available Literatures on Processing of Metal Oxides through Hydrogen Plasma

CHAPTER - 2

LITERATURE REVIEW

2.1. Bauxite Minerals:

India is 5th largest resources of bauxite in the world and comprises more than 3000 million ton resources. In the state of Gujarat high alumina, low iron, low titanium bauxite occurs and they are widely used for calcinations for refractory and abrasive industries. The high alumina bauxite of Orissa, Chhattisgarh, Madyapradesh, Jharkhand, and Maharashtra, generally has high titanium and also significant iron content. The bauxite reserve in the Orissa state is of the order of 1607 million tonnes which is approximately 52.9% of the country's total reserve [12]. World reserves of Bauxite are shown below;

Table 2.1: Bauxite reserves in the world (2012) [11]

Country	**Reserves (in '000 tons)**
World : Total (rounded)	29,000,000
India	**900,000**
Guinea	7,400,000
Australia	6,200,000
Brazil	3,600,000
Vietnam	2,100,000
Jamaica	2,000,000
China	830,000
Guyana	850,000
Greece	600,000
Suriname	580,000
Venezuela	320,000
Russia	200,000
Kazakhstan	160,000
USA	20,000
Other countries	3,300,000

Bauxite is an aluminous rock containing hydrated aluminium oxides as the major composition and iron oxide, silicon oxide and oxide of titanium in different quantities. Oxides of hydrated aluminium present in the bauxite are diaspora ($Al_2O_3.H_2O$) and gibbsite ($Al_2O_3.3H_2O$). Bauxite is a vital ore of aluminium which is one of the most important non ferrous materials used in the industry. It is also an essential ore for chemical and refractory industries. The different grades of bauxite according to their chemical composition are shown below;

Table 2.2: IS Specifications for Metallurgical Grade Bauxite [11]

Constituent	**% of Gr. I**	**% of Gr. II**
Al_2O_3	min 40	min 47
SiO_2	max 4	max 4
Module Al_2O_3/SiO_2	min 12	min 12
Fe_2O_3/TiO_2	max 30	max 30
P_2O_5	max 0.21	max 0.21
V_2O_5	max 0.22	max 0.19
LOI at 1100°C	20	20

Table 2.3: IS Specifications for Chemical and Petroleum Grade Bauxite [11]

Constituent	**Requirement**
Al_2O_3	min 58.0
SiO_2	max 3.0
Fe_2O_3	max 2.0
TiO_2	max 4.0
P_2O_5	max 0.3
MnO	max 0.1
CaO	max 2.1
Loss on ignition	max 30.0

Table 2.4: IS Specifications of Bauxite for Refractory Industry [11]

Constituent	Percent
Al_2O_3	58 min
Fe_2O_3	3 max
TiO_2	3 max
CaO	0.5 to 0.7
LOI	27-30

2.2. Aluminium production:

Aluminum oxide is very stable oxide with free energy change of formation is -252 Kcal/mol. The carbothermic reduction of aluminium oxide has not been commercially adopted for the reasons now listed below [10];

- It requires high temperature around 2000°C.
- At temperature 2000°C undesirable aluminium carbide is formed.
- The refractories required for operation at such temperature are not only expensive but are also not readily available.

Commercially, production of Aluminum metal from bauxite is a two stage process. The first stage is Bayer process for refining of bauxite ore resulting production of Alumina. The second stage is the Hall Heroult process, an electrolytic reduction of Alumina to Aluminum metal [7].

2.2.1. Bayer process

The Bayer process currently dominates world alumina production. By the Bayer process, high purity alumina is extracted from bauxite. In this process, bauxite is initially leached by NaOH, at high pressure (25atm) and high temperature (220°C) to form soluble sodium aluminate from which $Al(OH)_3$ is subsequently precipitated. When $Al(OH)_3$ is calcined, Al_2O_3 is obtained. The flow sheet and reactions are briefly explained below, as reported elsewhere [14].

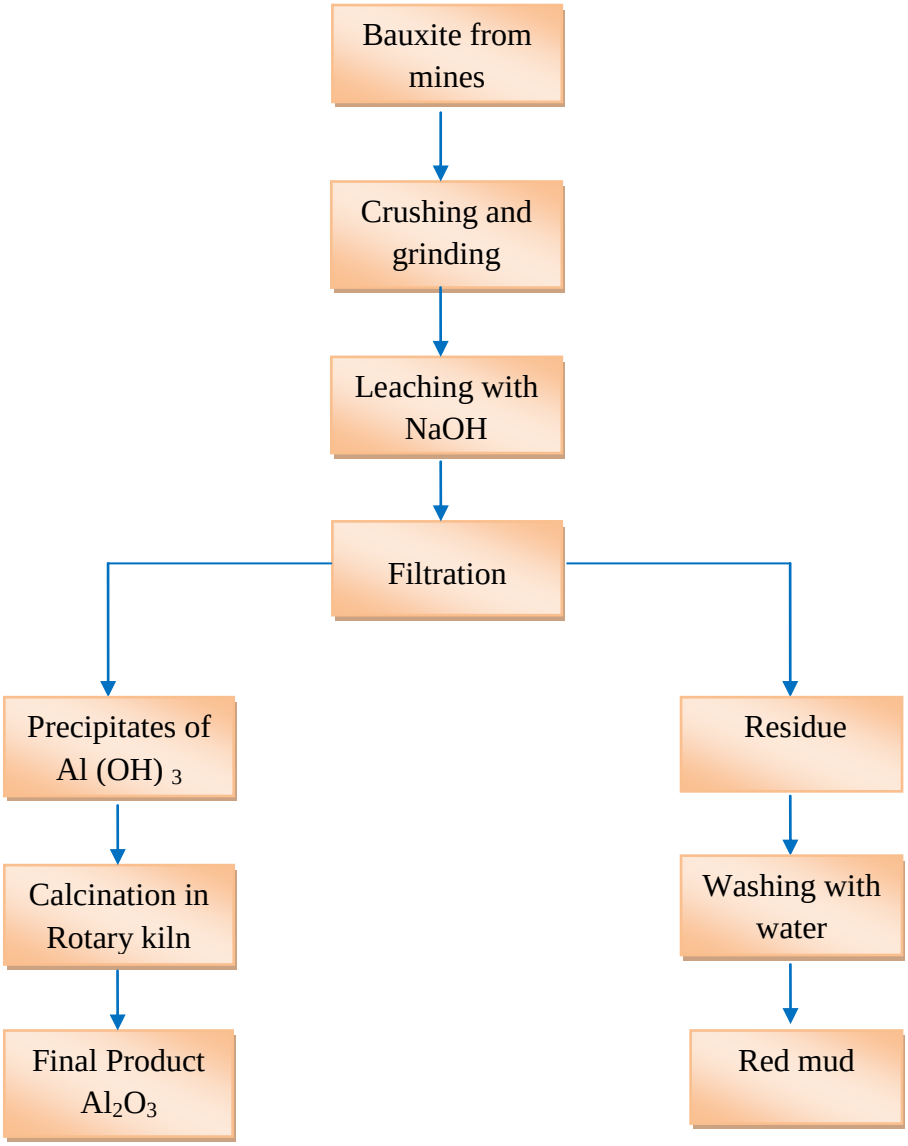


Fig. 2.1: Flow sheet of Bayer process.

First, the ground bauxite is mixed with recirculating strong NaOH at temp 240°C and pressure 35atm to form sodium aluminate.

$$Al_2O_3.xH_2O + 2NaOH \rightarrow 2NaAlO_2 + 2x.H_2O \quad \text{…….. (2.1)}$$

The NaOH will dissolve the amphoteric aluminium oxide but not the metal oxides impurities which are basic in nature. Sodium aluminate solution containing insoluble bauxite residues sink to the bottom (red mud). The impurities in the bauxite remain as solids all of these solids are separated from the solution of sodium aluminate by filtration. The solution was cooled

and treated by bubbling carbon dioxide into it, through which aluminium hydroxide precipitates.

$$2NaAlO_2 + 3H_2O + CO_2 \rightarrow 2Al(OH)_3 + Na_2CO_3 \quad \ldots\ldots\ldots\ldots\ldots\ldots (2.2)$$

In the last, $Al(OH)_3$ precipitates are washed to remove Na_2CO_3 and washed precipitate is then fed into a calciner maintained at temperature around 1500°C to produce the product Alumina. Calcination is done in rotary kiln.

$$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.3)$$

It is noted that, to produce 1 ton of Al_2O_3 by the Bayer process, required 2.2-2.4 tons of bauxite and 0.08-0.12 ton of caustic soda.

2.2.2. Hall-Heroult process

Hall-Heroult process is the only practical commercial method of production of aluminium and is based on the electrolytic decomposition of alumina [10]. Electrolytic cell for the electrolysis of alumina is shown in fig. 2.2. During operation the cell bath is filled with electrolyte and the anode is lowered into it. Electrolyte is an essentially molten cryolite, electrolysis medium contains excess AlF_3 (10-12%) and CaF_2 (4-6%) along with alumina. The additives increases the conductivity of the medium and lower the melting point of the cryolite from 1010°C to 920-970°C resulting in decrease in energy consumption. A current (50,000-100,000 amps) is passed through the cell circuit until the cryolite melts. When the bath attains a molten state, addition of alumina is started. Alumina is added to the electrolysis cell periodically because during the electrolysis its concentration drops, and if it is allowed to fall below about 2%, the electrolysis cell undergoes a sudden and major operational failure known as an 'anode effect' [7, 22].

The alumina decomposes to yield alumina and oxygen. The oxygen from the alumina is eliminated at the anode, while the alumina, being denser than cryolite, accumulates at the bottom of the box. The bath composition, temperature etc. have significant effect on the production of aluminium by Hall-Heroult's process [10].

All the reaction, which is a cause of aluminium production are shown below.

$$Na_3AlF_6 = NaAlF_4 + 2NaF \quad \ldots\ldots\ldots\ldots\ldots (2.4)$$

$$NaAlF_4 = NaF + AlF_3 \quad \text{……..... (2.5)}$$

$$12NaF + 2Al_2O_3 = 4AlF_3 + 6Na_2O \quad \text{…….. (2.6)}$$

$$6Na_2O = 12Na + 6O \quad \text{...…….... (2.7)}$$

$$12Na + 4AlF_3 = 12NaF + 4Al \quad \text{...……..... (2.8)}$$

$$6O + 6C = 6CO$$

$$\text{Or, } 6O + 3C = 3CO_2 \quad \text{...…… (2.9)}$$

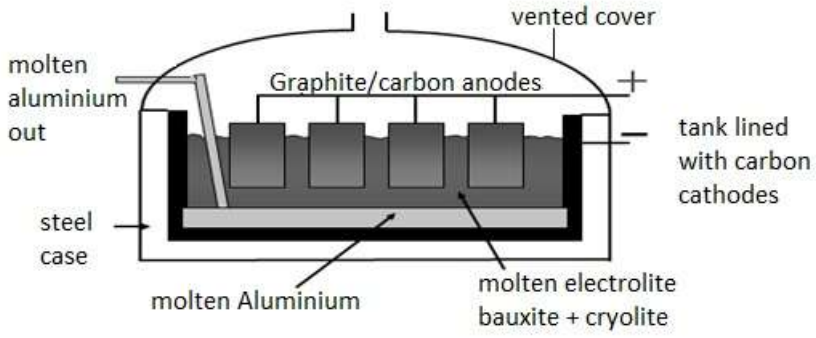


Fig. 2.2: Schematic diagram of Hall-Heroult process

2.2.3. Disadvantages in present Al Production (Bayer and Hall Heroult process)

- The hydrometallurgical effluents for the Bayer process and the fumes generated by the Hall-Heroult process constitute the major cause of pollution around plants. For example during the Bayer process a large no. of sodium ions are introduced during NaOH leaching and these ions are discharged from the system into the natural water resources [10].
- The disposal of red mud is also a serious problem.
- During the Hall-Heroult process fluorides, fluorine and sodium vapour are emitted as fumes from the aluminium electrolytic cells. The gaseous effluent destroys the vegetation around the plant site.
- The electrolysis process uses large amounts of energy in the extraction of reactive metals and makes aluminium expensive to produce.

- In Hall-Heroult process pure and expensive raw materials are used especially the aluminium oxides and anode carbon [21]. Electrodes are made up of graphite which is very expensive and a large number of electrodes are being used for the extraction of aluminium by Hall Heroult process.

2.3. Ellingham Diagram:

Ellingham diagram are graphical representation of ΔG^o (standard free energy change) Vs. T (temperature). For most metal oxides free energy of formation is negative, and so the diagram is drawn with $\Delta G=0$ at the top of the diagram, and the values of ΔG shown are all negative numbers.

- Gibb's Free Energy (ΔG): Energy of the system available to do work.

$$\Delta G = \Delta H - T.\ \Delta S$$

- ΔH: Energy that is liberated when the reaction occurs.
- ΔS: Entropy.

Spontaneity of a Chemical Reaction - "Natural tendency of occurrence" is called "spontaneous". A chemical reaction may or may not have a natural tendency to occur. If any reaction has this tendency to occur i.e. if it takes place spontaneously, the net Gibbs free energy (ΔG) of the reaction is negative. Spontaneity of the reaction at various ΔG values is shown in table below [10];

Table 2.5: Spontaneity of the reaction

ΔH	**ΔS**	**-TΔS**	**ΔG**	**Reaction characteristics**
-	+	-	-	Spontaneous at all temp.
+	-	+	+	Non-spontaneous at all temp.
-	-	+	+or-	Spontaneous at low temp., Non-spontaneous at high temp.
+	+	-	+or-	Spontaneous at high temp., Non spontaneous at low temp.

2.3.1. Properties of Ellingham diagram [5]

- All metal oxides curves slop upward- The slope of curve is $-\Delta s^o$ is a function of entropy of the products and reactant.

$$\Delta s^o = \sum s^o \text{ (product)} - \sum s^o \text{ (reactant)}$$

$$M + O_2 = MO_2$$

$$\Delta s^o = s^o \text{ (solid oxide)} - s^o \text{ (solid M)} - s^o (O_2 \text{ gas}) = -s^o$$

- The slope of most of the curves ($-\Delta s^o$) becomes positive. If mat. melt/vaporize the slop changes.

- Relative stability of oxides - Oxides which are lower most position in Ellingham diagram have more –ve ΔG^o values .hence they are the most stable oxides. Ex- CaO, MgO, Al_2O_3, ZrO_2. As we go down from top to bottom in the Ellingham dia. the ΔG values becomes more and more –ve and hence stability of oxides increase.

- Effect of temperature on stability of metal oxides - It is clear from the Ellingham dia. that as temp increases ΔG^o increases and hence the stability of the oxides decreases.

- Decomposition of metal oxides - On increasing temp the stability of oxides decreases and at a particular temp the metal-metal oxides line crosses the $\Delta G^o = 0$ line ,at this temp.(T_e) $\Delta G^o = 0$ so equilibrium is established i.e. neither the oxidation of metal nor the decomposition of metal oxide will occur, so this temp is called Decomposition temp of metal oxides. When the curve crosses $\Delta G^o = 0$ line decomposition of oxides.
  When $T > T_e$ decomposition of metal oxides takes place

- Any metal will reduce the oxide of other metal which is above in Ellingham diagram.

- Behaviors of CO_2 and CO lines,

$$C + O_2 = CO_2$$

$$\Delta s^o = s^o \text{ (1 mol of } CO_2 \text{ gas)} - s^o \text{ (1 mol of solid C)} - s^o \text{ (1 mol of } O_2 \text{ gas)} = 0$$

Thus the line becomes horizontal.

$$2C + O_2 = 2CO$$

$\Delta s^o = s^o$ (2 mol of CO) - s^o(2 mol of C) - s^o (1 mol of O_2) = positive

Thus the slope of line ($-\Delta s^o$) becomes negative.

- The lines of ΔG^o for CO and CO2 crosses at about 700°C.hence CO is more stable than CO2 at temp higher than 700°C.

2.3.2. Applications of Ellingham Diagram

Ellingham diagram has following applications;

- At different temperatures a graphical and qualitative visualization of the ease of reduction of oxides with a reducing agent.
- Ellingham diagram provides the information about using other reducing agents (for which the $\Delta G°$ value is present).
- It suggest about optimum temperature for extraction of metal with a reducing agent.
- This diagram gives an idea of the reactions taking place at different temperatures during heating of the oxides with the reducing agent.

2.4. Plasma:

Plasma is ionised gas, i.e. it contains, ions, electrons, neutral atoms and/or molecules. Plasma contains some properties of gases, but differs from gases in being good conductors of electricity and being affected by magnetic fields. [23]. Gases commonly used for treatment of plasma are chemically inert (He and Ar), reactive and polymerisable (NH_3, air, H_2) [8].

For industrial processes the plasma technology essentially uses two different types of plasma; the first one is non-equilibrium plasma or cold plasmas, more popularly known as glow-discharge plasmas. It is low-pressure plasma characterized by high electron temperatures (T_e) and low ion & neutral particle temperatures (T_i). They are widely used in lighting, etching, , film deposition, surface cleaning and polymerization [13]. Plasma is produced under vacuum conditions using low power radio frequency (rf) or microwave or dc sources [9]. The second type of plasma is thermal plasmas or hot plasmas are characterized by the electron temperature being approximately equal to the gas temperature (T_g) and the plasma is said to be in local thermal equilibrium. Normally, plasmas in the temperature range of 2,000-30,000 K and with charged particle density of 10^{19} - 10^{21} m^{-3} are termed thermal plasmas. Thermal plasma processing has been successfully applied to develop advanced ceramic coatings, synthesis of nanocrystalline materials, processing of minerals and ores and treatment of hazardous wastes [10].

2.4.1. Plasma generation

Plasma is mainly generated by passing an electric current through a gas. While a gas at room temperature is an excellent insulator, a small percentage of charge carriers, ions and electrons can be sufficient to make the gas electrically conducting. Plasma comprises molecules, atoms, ions, electrons and photons. However, overall it is electrically neutral [4]. When a sufficient large voltage is applied across a gap containing a gas or gas mixture, it will break down and conduct electricity. The reason is that the electrically neutral atoms or molecules of the gas have been ionised i.e. split into positively charged ions and negatively charged electrons. The nature of break down and the voltage at which this occurs varies with the gas pressure, gas flow rate, gas species, material, the separation distance of the electrodes, the nature of high voltage supply. The interaction of the electrically charged particles with the neutral gas, with each other and with contact surface produces the unique chemical and physical properties of the plasma environment. This environment is different from that found in solids, liquids and gases hence plasmas are sometimes called the forth state of matter [8].

2.4.2. Application of Plasma

Now plasma technologies are being employed in different areas to overcome the problems of conventional methods and developing new methods with higher efficiencies. The different categories of plasmas and their applications are listed in Table below;

Table 2.6: Category of plasma [10]

Category of plasma	Applications
Low-pressure plasmas (10^{-4} - 10^{-2} torr) & ($T_e > T_i > T_g$)	Sputtering and surface modification processes, plasma source for ion implantation
Medium pressure plasmas (10^{-2} - 1 torr) & ($T_e > T_i = T_g$)	Etching, microelectronic processing
Sub atmospheric pressure plasmas (1- 100 torr) & ($T_e > \sim T_i = T_g$)	**Plasma chemistry**, plasma polymerization
Atmospheric plasmas (100+ torr) & ($T_e = T_i = T_g$)	Plasma spraying, plasma melting, material synthesis

2.4.3. Hydrogen plasma

In plasma metallurgy, hydrogen can be chosen as a reducing gas for ore reduction purposes. Hydrogen under ambient temperature exists only in its molecular form (H_2) where the covalent bond between the two atoms is secured by a shared electron pair. At higher temperature H_2 starts to dissociate, as shown in figure 2.3, where the amount of H exceeds that of H_2 at approximately 3500°C. Increasing the temperature furthermore leads to the ionisation of H into H^+. H^+ exceeds H at a temperature of 15500°C [4]. There are several methods known to dissociate molecular hydrogen like ultraviolet radiation, thermal or electrical energies etc. A graph between Hydrogen dissociation & ionisation and temperature are shown in figure 2.3.

The major disadvantage of the plasma process lies in the use of electricity as energy source, which unfavorably affects the process economy. And another disadvantage is that the plasma processes have more parameters to control as compared to traditional processes and therefore requires a higher degree of automation in the process control [9].

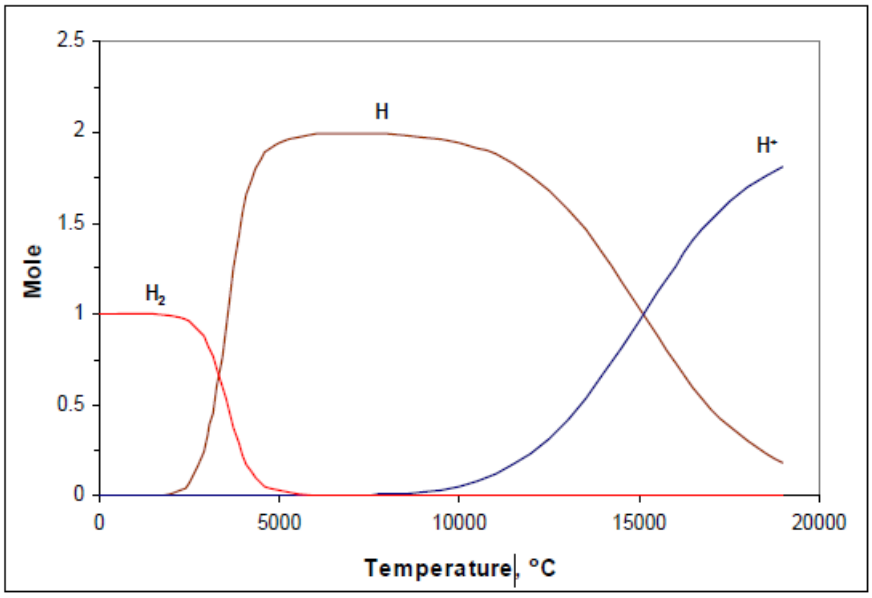


Fig. 2.3: Hydrogen dissociation and ionisation versus temperature [4]

2.5. Available Literatures on Processing of Metal Oxides through Hydrogen Plasma:

A. A. Bergh, [2] found that atomic hydrogen can be used for reduction of oxides as reducing agent at lower temperature compared to molecular hydrogen. Atomic hydrogen is electrically neutral and is not subjected to shielding effect. Reduction temperature in both molecular and atomic hydrogen was developed for different oxides and in case of atomic hydrogen was found to be substantial lower. Reduction temperature for the atomic hydrogen was determined by the color changes of oxides.

W. Zhang, et al [4] investigate the deoxidation of partially oxidized titanium by hydrogen plasma. Various attempts to reduce TiO_2 using hydrogen plasma have obtained in which TiO is best. The re-oxidation by the water vapour, by-product may be one of the mechanisms responsible for limiting reduction. In an effort to improve the understanding of the reduction mechanisms, coupons of titanium metal were partially oxidized and then exposed to a hydrogen plasma environment. Experimental results have shown that thicker oxide layers were reduced to a greater extent than thinner layers, indicating that the close proximity of titanium is a hindrance to hydrogen reduction of titanium dioxide.

B. Bhoi, et al [13] studied for preparation of direct reduced iron through hydrogen plasma. 5 different samples of iron ore were reduced by hydrogen plasma, by varying flow rate power input and temperature. First iron ore sample was kept onto the sample holder and then evacuating the chamber with flow rate 100-500 sccm followed by heating the holder and sample at temperature 300-800°C, pressure 20-100 torr and power input 500-1500 watt. After reduction process the sample was cooled by hydrogen at flow rate of 300 sccm. Then analyzed its chemical composition by wet chemical analysis and X-ray diffraction technique and observed that 99% metallization is achieved and only iron peaks appeared in XRD result. Advantages suggested by B. Bhoi in this invention are given below;

- Iron ore reduction by plasma is environment friendly means no production of CO and CO_2 gas.
- Carbon bearing material did not use and no preheating of materials.
- Conventional method of iron production involves many processes like Sintering, Pelletization and coke making but plasma process utilizes only one stage.

R. A. Palmer, et al [15] performed experiment on TiO_2 reduction with hydrogen plasma. The plasma gas composition was 50% H_2 and 50% Ar. Experiments were performed using a range of processing times and different quantities of TiO_2. He observed that processing time, gas purity and TiO_2 mass have less effect on the degree of reduction. Hydrogen plasma reduction of TiO_2 was potential method for the production of Ti-O with titanium content between 67% - 73%. Atomic hydrogen did not significantly influence the extent of reduction. This implies that the present experiment technique is not suited to producing metallic Ti.

Damien Wagner, et al [16] studied the reduction of pure hematite by hydrogen at laboratory scale. Reduction experiment was carried out at setaram TAG 24 (thermobalance). Gases used were hydrogen argon and helium. Hydrogen is a reacting gas and argon & helium are carrier gas. At the end of experiment hydrogen valve was closed and argon was blown into the balance so as to expel the hydrogen and supply helium until get to room temperature. XRD analysis shows some sample appears magnetite, some sample appears iron particles, and the last sample is composed of pure iron. For some of them SEM were taken. Reduction from wustite to iron dramatic changes in the morphology of the particles, the iron phase could clearly observe in the last sample.

Herbert L Gilles, et al [17] performed an experiment on reduction of iron ore in a dc plasma jet and studied the effect of power input, reducing gas concentration, and particle size. Ore was injected into the plasma from the anode orifice and the reduced product collected in a chamber of water quenching. Reduction decreased with increasing ore size and increased with greater energy in the plasma. XRD analysis and microscopic examination of the collected product shows physical and chemical changes as the amount of reduction varied. Finally it is found that the modified anode with feed ports at a 45° angle is the most satisfactory ore injection approach. The ore and collected product were examined by spectroscopic techniques and wet chemical for iron-bearing material. The oxygen content of the product and ore was found as the difference between the weight of sample and the weight of all other measured elements.

Takayuki Watanabe, et al [18] studied the reduction of a SiO_2-Al_2O_3 mixture with thermal plasma for metal production. In the reduction of the SiO_2-Al_2O_3 mixture atomic hydrogen plays an important role. For the treatment of the SiO_2-Al_2O_3 mixture argon and argon-hydrogen plasma jets were used with different compositions. The evaporated species as the fumes were identified by XRD technique and energy dispersive X-ray spectrometry (EDS).

After the treatment the weight loss was measured to determine the evaporation amount from the sample. The argon plasma produces SiO and gaseous silicon from the mixture of SiO_2-Al_2O_3, while Al_2O_3 has not been reduced. The argon-hydrogen plasma produces mainly gaseous silicon with some amount of gaseous SiO and Al. Both of the argon and the argon-hydrogen plasmas produce the silicon component collected as the fumes having the purity of 98-99% from the mixture of SiO_2-Al_2O_3.

T Maki, et al [19] performed a reduction experiment of Fe_3O_4 nanoparticles coated with oleic acid as a surfactant with hydrogen plasma. Radio-Frequency (RF) of 13.56MHz was applied to generated hydrogen plasma. With higher power input of Radio-Frequency to the inductive coil, nanoparticles of Fe_3O_4 could be transformed to almost single phase of Fe_3C and finally to α-Fe. The input Radio-Frequency power for generating plasma was varied from 50W to 450W and the hydrogen gas pressure & the duration of treatment were fixed at 6Pa and 1h, respectively. Crystal structure of nanoparticles was analyzed by XRD technique. It is found that the hydrogen plasma treatment may be useful to regulate the phase formation in iron based nanoparticles.

Daniel E Bullard and David C lynch [20] investigated the reduction of TiO_2 in a moderate-pressure (p < 46 torr) with nonequilibrium hydrogen plasma at temperatures 1273K. The effect of plasma pressure, plasma power, applied voltage, and processing time was examined. Using a packed bed specimen, TiO_2 at the surface in contact with the plasma was reduced to Ti_2O_3 at temperatures below 1273 K. After 5 to 10 minutes of reaction 60 wt% of the surface material was converted to Ti_2O_3. Where the plasma does not reach, H_2 reacts with TiO_2 and produces $Ti_{50}O_{99}$. After all the TiO_2 conversion to $Ti_{50}O_{99}$, the wt% of TiO_2 in the surface material goes to zero and Ti_2O_3 concentration starts to decrease. It is found that this decrease in the wt% of Ti_2O_3 is concern with production of another oxide between Ti_2O_3 and TiO.

CHAPTER-3

MATERIALS AND METHOD

3.1. Material used

3.2. Experimental apparatus

3.3. Experimental Procedure

CHAPTER - 3

MATERIALS AND METHOD

3.1. Material used:

Bauxite sample was provided by **NALCO** and the chemical composition of supplied bauxite ore is given below;

Table 3.1: Chemical composition of Bauxite ore (wt %)

Al_2O_3	Fe_2O_3	TiO_2	SiO_2	LOI
43%	23%	3%	4%	22.5%

From the above table it is clear that the supplied sample has highest Al_2O_3 wt% as compared to other oxides. The loss of ignition was found 22.3% from our experiment which is approximately same with given LOI data.

3.2. Experimental Apparatus:

3.2.1. Planetary Ball Mill

These mills are also referred as centrifugal mills and are used to grind samples into fine powder by high grinding energy. This apparatus used for sample preparation to form fine powder of bauxite.

Fig. 3.1 shows a 4 station planetary ball mill presented by Gilson Company. The samples are kept in one of the vile and various balls are added. The vile is covered by the cover plate and then it is placed in the machine. Once the viles are placed and secured, the mill begins to function. The bowls are independent of the rotating platform and the direction of bowls rotation is opposite to the direction of the platform. Causing of alternate addition and subtraction of the centrifugal force, the grinding balls rotate halfway in the vile and then thrown across the viles and then impacting the opposite walls at very high speeds. Here used 300 rpm of revolution and time taken was 1hr.

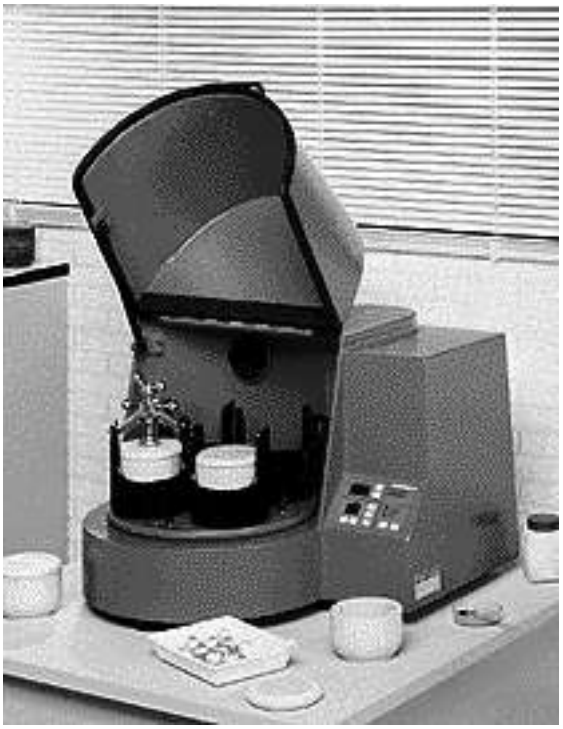


Fig. 3.1: A four station planetary ball mill

3.2.2. Pelletizer Machine

The bauxite powder is pelletized in a uni-axial cold compaction machine with a load of 6 ton, where the bauxite powder is compacted to obtain cylindrical pellets of 20mm diameter and 4mm thickness. The compaction machine is shown below;

Fig. 3.2: Pelletizer machine

3.2.3. Hydrogen Plasma Reactor

Hydrogen plasma processing was carried out with microwave hydrogen plasma reactor at **IMMT Bhubaneswar**. The reactor is shown below;

Fig. 3.3: Microwave Hydrogen Plasma reactor

3.2.4. XRD (X-ray diffraction) Phase Analysis

XRD technique was used to identify the different phases present in the sample. XRD analysis was done using Panalytical MPD system. The XRD patterns obtained from different samples were analyzed through commercial software, X-pert high score.

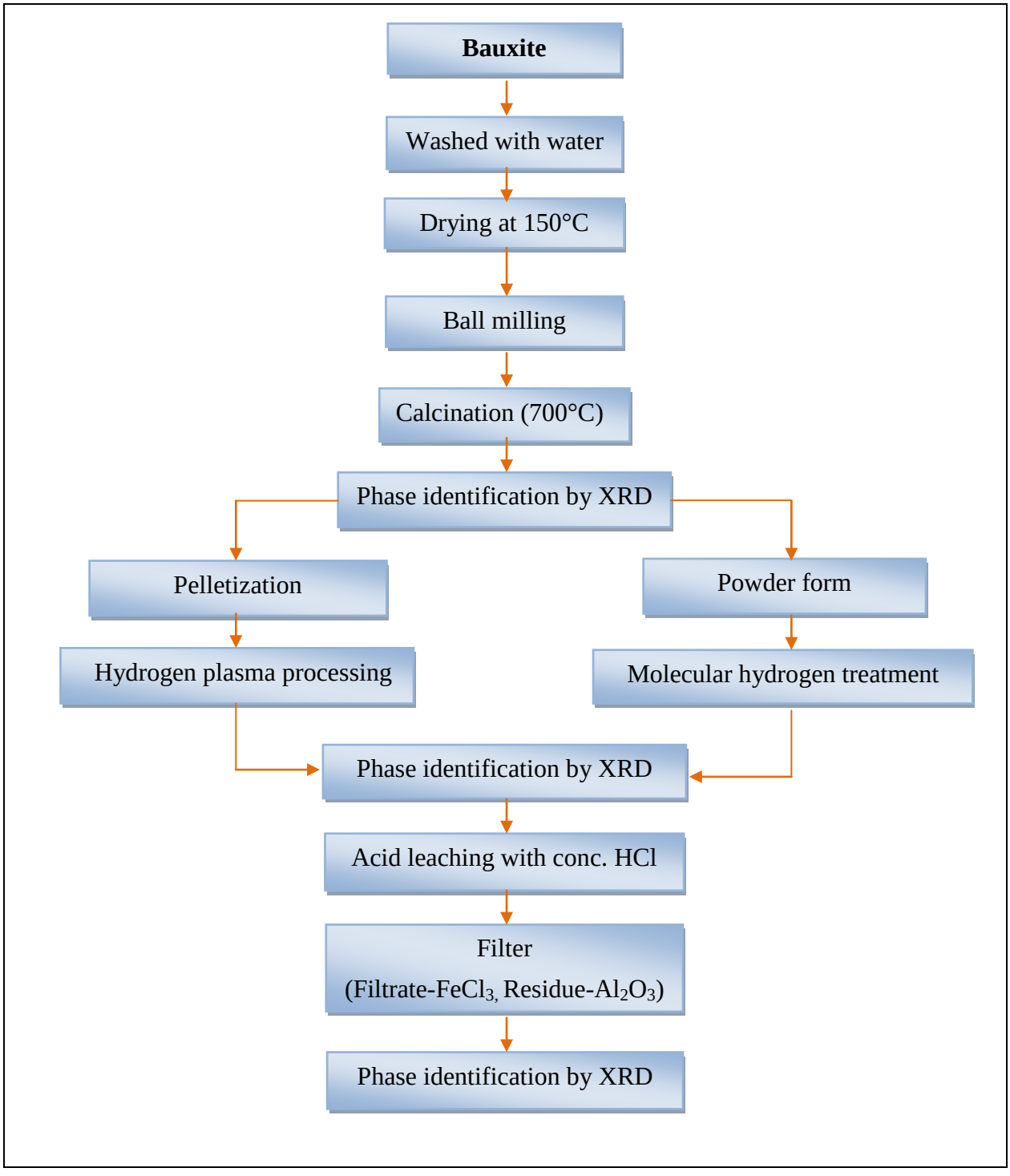
Fig. 3.4: X-ray Diffraction Machine.

3.3. Experimental Procedure:

3.3.1. Work plan

Sample preparation and processing of bauxite with hydrogen plasma and molecular hydrogen are done in the following manner;

Table 3.2: Flow sheet for sample preparation and processing



3.3.2. Experiment with Molecular Hydrogen

Sample Preparation

The lumpy mass of bauxite sample was kept in water for overnight and then washed with water to remove water soluble impurities. Washed sample was dried in oven for two hours at 150^0C for removing water contained by sample. The dried bauxite samples were subjected to ball milling to make fine powder for one hour and subsequently powdered bauxite sample was calcined at temperature 500°C-700^0C for 2-4 hours. XRD was carried out to know the various phases present in that calcined sample and analyzed the phases.

Molecular Hydrogen Treatment

Calcined bauxite sample was reduced by hydrogen (H_2) and the reduction was performed at SLM Metal (P) Ltd Rourkela. The calcined powder was subjected to hydrogen gas at 650^oC with 1.5Nm^3/hr flow rate for 1hr 15min and 2Nm^3/hr for 1hr 30min. Then XRD was carried out to know the various phases present in processed sample.

3.3.3. Experiment with Hydrogen Plasma

Sample Preparation

X-ray diffraction (XRD) on calcined bauxite powder sample was carried out to know the various phases present in sample. From the calcined bauxite powder pellets of 20mm diameter and 4mm thick were prepared by uniaxial cold compaction machine.

Fig. 3.5: Pellet of bauxite powder with 20mm dia. and 4mm thick

Hydrogen Plasma Processing

Hydrogen plasma processing was carried out with microwave hydrogen plasma reactor at **IMMT Bhubaneswar**. The plasma gas used was pure hydrogen. First maintain evacuation of the chamber, introduction of hydrogen gas, heating of holder and sample and then maintaining of plasma at the required power level. The system pressure, temperature, hydrogen flow and power were increased sequentially to reach the final power. The bauxite pellet was subjected to hydrogen plasma at temperature 650^{o}C and pressure 100 torr with hydrogen flow rate of 400sccm, 450sccm and 500sccm for 1hr 30min, 1hr 45min and 2hrs respectively. Hydrogen plasma system is shown below;

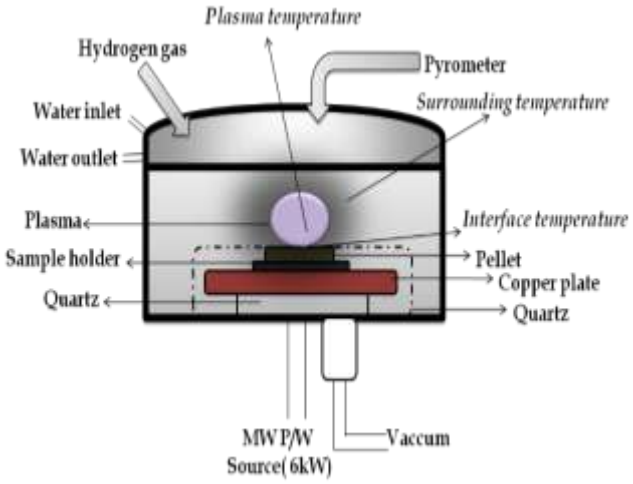


Fig. 3.6: Schematic diagram of Hydrogen Plasma System

Phase identification

XRD (X-ray diffraction) technique was used to identify the different phases present in processed sample. Processed sample was crushed, ground and then the phases present in that sample were analyzed by XRD.

3.3.4. Separation of iron constituents by Acid Leaching

Reduced bauxite sample with molecular hydrogen and hydrogen plasma was further leached with concentrated hydrochloric acid for overnight for the separation of iron from alumina. During acid leaching processed bauxite sample was added with concentrated hydrochloric acid and then the solution was filtered. Filtrate was treated with sodium hydroxides for the precipitation of iron hydroxide $(Fe(OH)_3)$ and the residue part was washed with distilled water and XRD was carried out to know the various phases present in the residue part.

CHAPTER - 4

RESULT AND DISCUSSION

4.1. Calcination studies

4.2. Reduction studies

4.3. Acid Leaching studies

CHAPTER – 4

RESULT AND DISCUSSION

4.1. Calcination Studies:

To study the effect of calcination time and temperature for treatment of bauxite with molecular hydrogen and hydrogen plasma, powder samples of bauxite were calcined at varying temperatures ranging from 500 to 700°C and for different time periods ranging from 2 to 4 hrs. Weight loss at 500°C for 2 hrs was found to be 17.50%, at 600°C for 2 hrs was found to be 19%, at 700°C for 2 hrs was found to be 21.2%, and at 700°C for 4 hrs was found to be 22.3%.

The difference in wt% of loss on ignition was due to presence of moisture, suspended water particle and other volatile impurities within the sample. For that purpose the calcination temperature were increased from 500 to 700°C for the removal of above given impurities. Effect of wt. loss with calcination temperature and time are shown in fig. 4.1. The graph shows, wt. loss increases with both temperature and time.

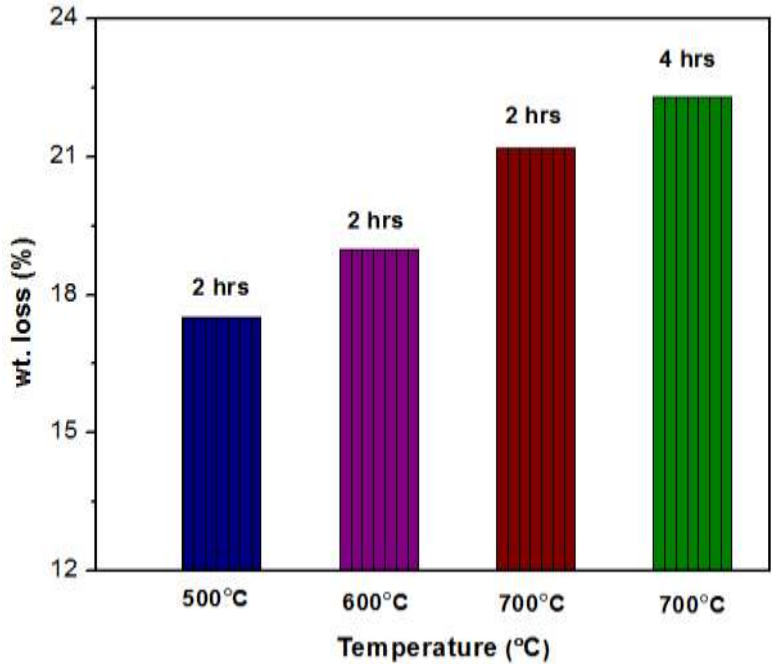


Fig. 4.1: Wt. loss of bauxite powder on ignition at different temperatures and time periods

4.2. Reduction Studies:

4.2.1. Reduction with Molecular Hydrogen

XRD phase analysis of treated calcined bauxite powder with molecular hydrogen emerges the different phases of iron and alumina. XRD plot before and after molecular hydrogen treatments are given in fig. 4.2 and fig. 4.3 respectively.

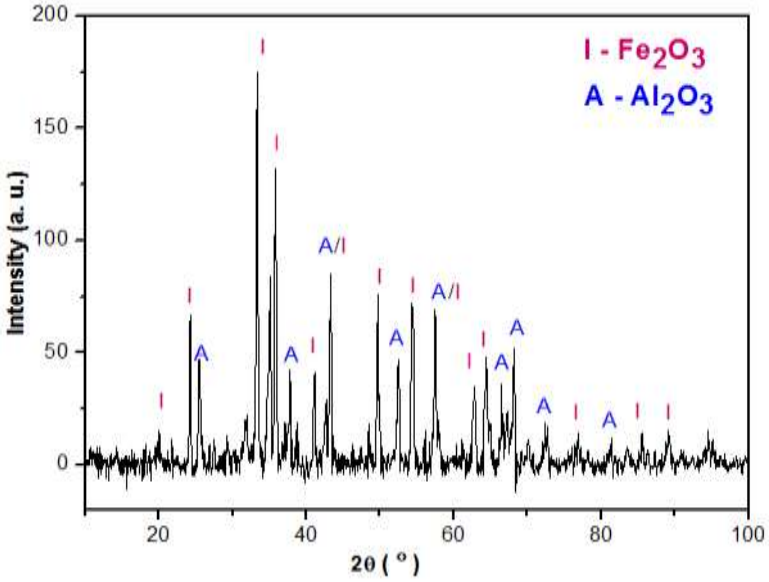


Fig. 4.2: XRD pattern of calcined bauxite before molecular hydrogen processing

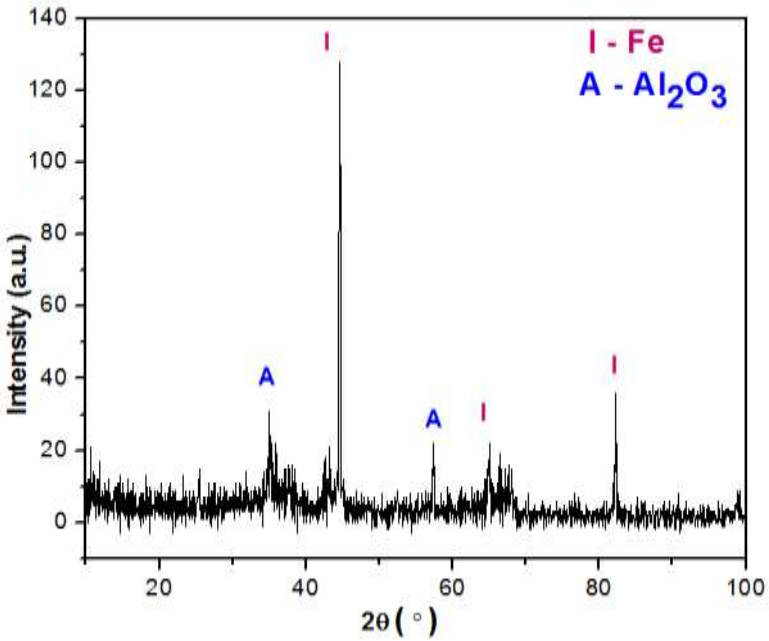


Fig. 4.3: XRD pattern of calcined bauxite after molecular hydrogen processing at 650^{o}C with hydrogen flow rate of 1.5 Nm^3/hr for 1hr 15min

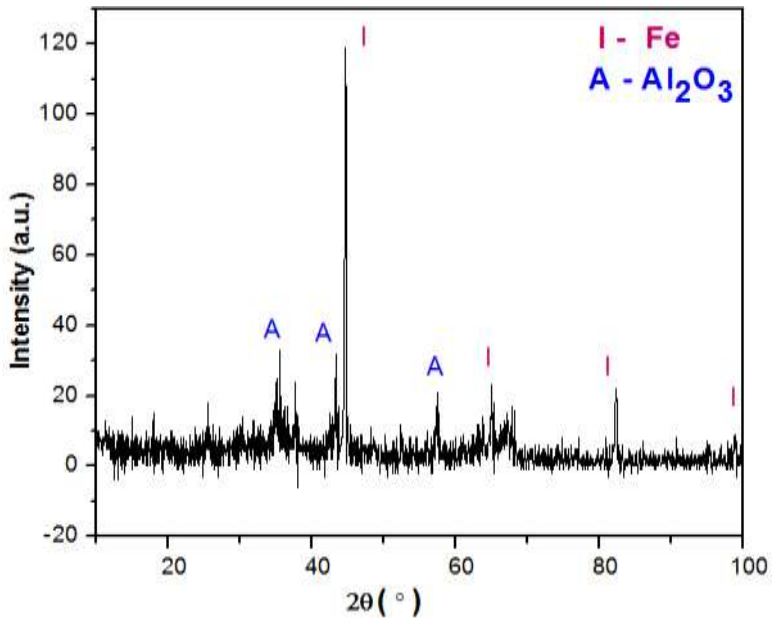


Fig. 4.4: XRD pattern of calcined bauxite after molecular hydrogen processing at 650^{o}C with hydrogen flow rate of 2 Nm^{3}/hr for 1hr 30min

The reduction of iron with molecular hydrogen can be understood easily by Ellingham diagram. The free energy change of formation of Fe_2O_3 is -95Kcal/mol and for molecular hydrogen reaction is -114.35Kcal/mol [3]. With the analysis of free energies it is clear that molecular hydrogen can reduce Fe_2O_3 only because of less free energy (-95Kcal/mol) as compared to Al_2O_3, SiO_2 and TiO_2. The possible reactions for the reduction of Fe_2O_3 are shown below [6];

$$3Fe_2O_3 + H_2 = 2Fe_3O_4 + H_2O \quad \text{..... (4.1)}$$

$$Fe_3O_4 + H_2 = 3FeO + H_2O \quad \text{..... (4.2)}$$

$$FeO + H_2 = Fe + H_2O \quad \text{..... (4.3)}$$

4.2.2. Reduction with Hydrogen Plasma

XRD peak analysis of hydrogen plasma treated bauxite pellets reveals the presence of various phases like Fe, Al_2O_3, SiO_2 and TiO_2. XRD plot of bauxite pellets before and after hydrogen plasma treatment are shown below;

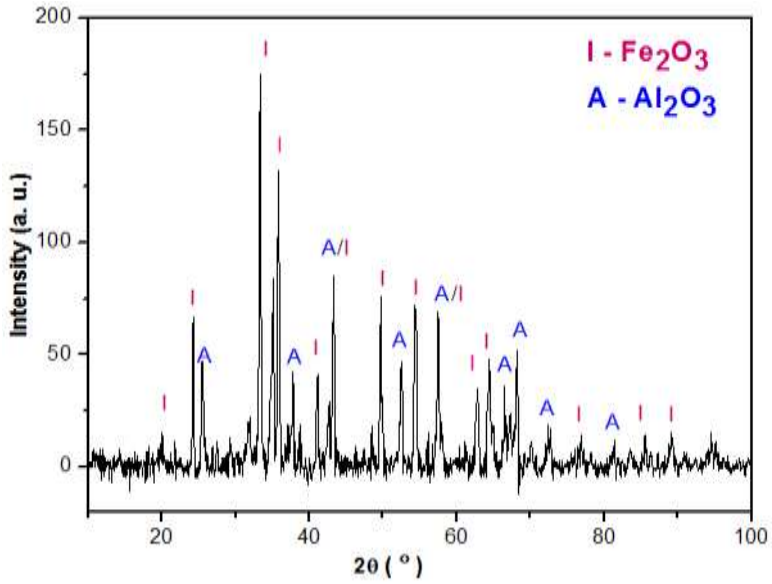


Fig. 4.5: XRD pattern of calcined bauxite before hydrogen plasma processing

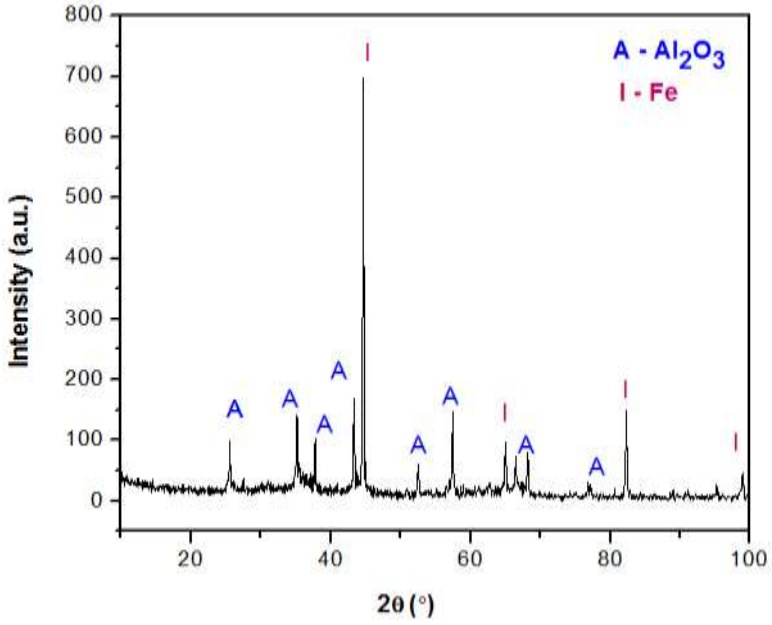


Fig. 4.6: XRD pattern of bauxite after hydrogen plasma processing at 650^{o}C with hydrogen flow rate of 400sccm for 1hr 30min

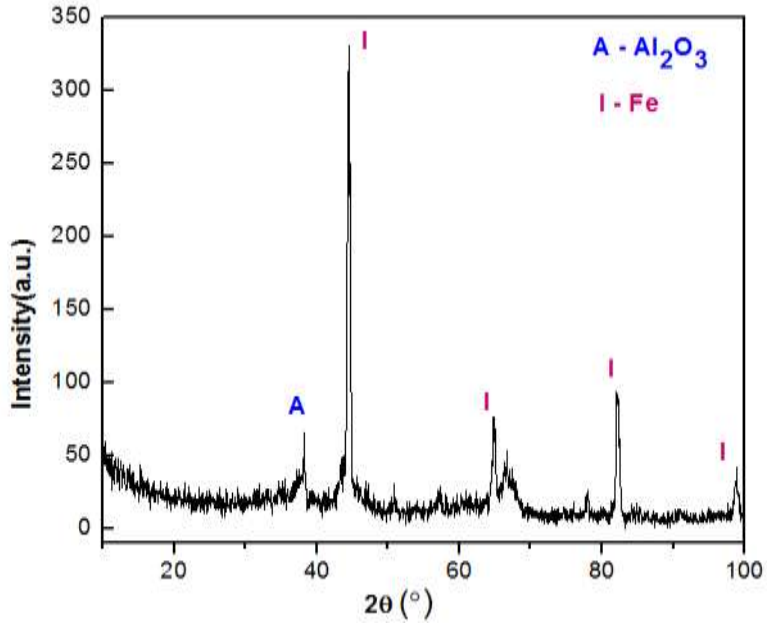


Fig. 4.7: XRD pattern of bauxite after hydrogen plasma processing at 650^{o}C with hydrogen flow rate of 450sccm for 1hr 45min

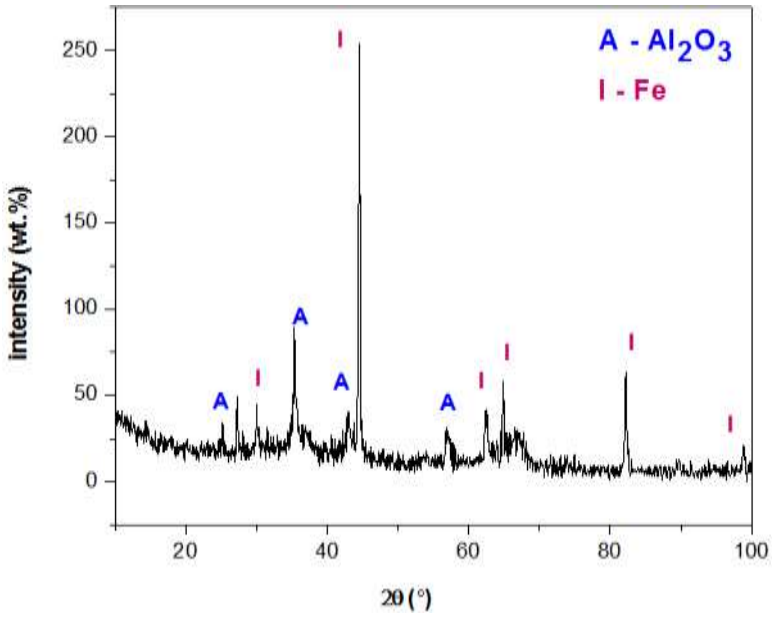


Fig. 4.8: XRD pattern of bauxite after hydrogen plasma processing at 650^{o}C with hydrogen flow rate of 500sccm for 2hrs

From the above XRD peak analysis it is observed that oxide of iron reduced to iron with the treatment of hydrogen plasma, but the other oxides present in bauxite are remained as such as before. Reduction of iron can be explained on the basis of Ellingham diagram. Oxides of iron

curve lying above in the Ellingham diagram as compared to other oxides present in bauxite like Al_2O_3, SiO_2 and TiO_2. According to Ellingham diagram, free energy change of formation of Fe_2O_3, SiO_2, TiO_2 and Al_2O_3 are -95Kcal/mol, -203Kcal/mol, -205Kcal/mol, and -252Kcal/mol respectively. With the comparison of free energies of above oxides it is clear that Fe_2O_3 is less stable as compared to others oxides. The reduction possibility of Fe_2O_3 with hydrogen plasma is more as compared to Al_2O_3, SiO_2 and TiO_2, hence Fe_2O_3 reduced to iron. It is also observed that by the analysis of XRD plots, higher flow rate (500sccm) of hydrogen has more iron picks. The possible reactions for the reduction of Fe_2O_3 with the hydrogen plasma are shown below [13];

$$H_2 = H + H = 2H = 2H^+ + 2e^- \quad \text{..... (4.4)}$$

$$Fe_2O_3 + 6H = 2Fe + 3H_2O \quad \text{..... (4.5)}$$

$$Fe_2O_3 + 6H^+ = 2Fe + 3H_2O \quad \text{..... (4.6)}$$

4.3. Acid Leaching Studies:

During the acid leaching process of reduced bauxite sample (with hydrogen plasma and molecular hydrogen), iron constituents was separated from the reduced sample. After filtration of the leached sample, filtrate contains chlorides of iron and residue contains alumina along with other oxides. Then the filtrate was treated with sodium hydroxides for the precipitation of iron hydroxide ($Fe(OH)_3$) and further heating of $Fe(OH)_3$ converted to Fe_2O_3. The possible reactions of reduced bauxite sample with concentrated hydrochloric acid are given below;

$$\text{Bauxite} + \text{conc. HCl} \longrightarrow \underset{\text{(Residue)}}{Al_2O_3} + \underset{\text{(Yellow colour)}}{\text{Chlorides of iron}} \quad \text{..... (4.7)}$$

$$\underset{\text{(Yellow colour)}}{FeCl_3} + \underset{\text{(Colour less)}}{3NaOH} \longrightarrow \underset{\text{(Colour less)}}{3NaCl} + \underset{\text{(Reddish brown precipitates)}}{Fe(OH)_3} \quad \text{..... (4.8)}$$

$$Fe(OH)_3 \xrightarrow{\Delta} Fe_2O_3 \quad \text{..... (4.9)}$$

The residue part was analysed by XRD and the XRD plot of residue part after leaching is shown in fig. 4.9. From the XRD plot it is clear that alumina phases are present in residual part after acid leaching.

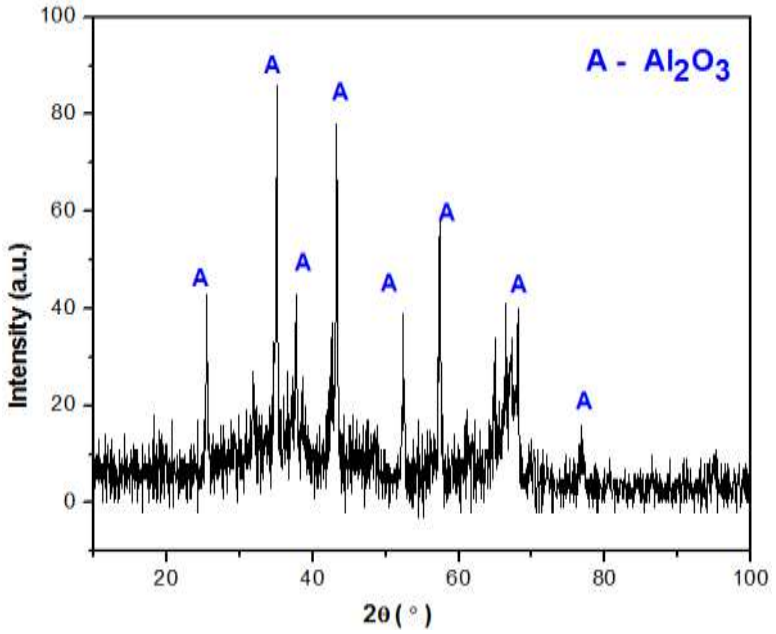


Fig. 4.9: XRD pattern of acid leached residual part

CHAPTER-5

SUMMARY

5.1. Summary

5.2. Scope for the future work

CHAPTER - 5

SUMMARY

5.1. Summary:

From the present investigation we can summarize the followings;

- On consideration of Ellingham diagram, all metal oxides present in bauxite should have reduced to their respective metals with the treatment of hydrogen plasma, but our present work reveals only the reduction of iron oxide to iron is possible with the experimental parameters like hydrogen flow rate (400sccm for 1hr 30min, 450sccm for 1hr 45 min and 500sccm for 2hrs), temperature (650°C) & pressure (100torr) and other oxides present in bauxite like Al_2O_3, SiO_2 and TiO_2 are found to be unreduced.

- In our further study, we have also investigated bauxite sample with molecular hydrogen and observed that only iron oxide is reduced to iron under the processing conditions (hydrogen flow rate 1.5 Nm3/hr for 1 hr 15 min and 2 Nm3/hr for 1hr 30min).

- Iron constituent has been successfully separated from the reduced bauxite sample by acid leaching process.

5.2. Scope for the future work:

The reduction of various oxides present in bauxite like Al_2O_3, Fe_2O_3, SiO_2 and TiO_2 are thermodynamically possible with hydrogen plasma (ionic hydrogen, atomic hydrogen). But the present work reveals that only the reduction of iron oxides to iron is possible through hydrogen plasma.

Changing the process parameters like increased flow rate of hydrogen, reduction temperature, operating pressure and duration of reduction, may be helpful for the successful reduction of alumina. In the present time frame and limited source of experimental facility on hydrogen plasma, the authors couldn't extend the investigation. In future if such a reduction process is possible then we can obtain a method of eco-friendly (because of no input of carbon), lower cost of aluminium extraction.

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